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"INFLUENCE OF STEREOCHEMISTRY ON RADIATION-INDUCED
STRUCTURAL CHANGES IN PMMA"

by

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) We have been studying the effects of radiation on poly(methylmethacrylate), PMMA, which has been used as a resist in computer chip microlithography. In contrast to predictions based on solution photochemistry of related compounds we have found by careful spectroscopic study of the irradiated polymer leads to four different kinds of double bonds. These ester cleavage reactions do not necessarily lead to rupture of the backbone, a necessary condition for efficient use as a resist. We find evidence that not only does the state (solution vs. film) upon which irradiation is carried out affect the product distribution, but also that the stereochemistry of PMMA (atactic vs. isotactic) plays a role.				
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INFLUENCE OF STEREOCHEMISTRY ON RADIATION-INDUCED STRUCTURAL CHANGES IN PMMA

by

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INTRODUCTION

Exposure of poly(methyl methacrylate), PMMA, to radiation sources such as ultraviolet, x-ray, electron and proton beams results in reduced molecular weight,¹ the evolution of gaseous products,² the generation of unsaturated bonds by the scission of side chains,^{3, 4} and the appearance of the characteristic electron spin spectra of radicals.^{2, 5} These changes in PMMA films caused by irradiation with these sources increase the solubility in the exposed area, permitting PMMA to be used as a resist in advanced microlithography.

The chemical changes in irradiated PMMA films as measured by gel permeation chromatography, Fourier-transformed infrared and UV spectroscopies demonstrated a 1:1 correspondence between the disappearance of ester groups and the generation of double bonds in the polymer chain by UV and high energy radiations (x-ray, electron and proton beams). The comparison of the ratio of main chain scission to changes in the number of ester groups indicated that high energy radiation was about 10 times more efficient than deep UV in causing main chain scission with less ester group removal. The unsaturated bonds associated with main chain scission were much more pronounced in the ¹H NMR spectra of PMMA exposed to high energy radiations.⁴

In this work, we extend the analysis of our earlier results to include examination of the changes in the stereochemical triad sequences in the UV-irradiated PMMA. In addition, structural changes in isotactic PMMA films and solutions of atactic PMMA by UV-exposures are reported.

EXPERIMENTAL

Materials and Sample Preparation

Atactic PMMA, Du Pont Elvacite 2041, was purified by reprecipitation from toluene into methanol and dried in a vacuum oven ($M_n = 1.76 \times 10^5$ g/mole from GPC measurements with polystyrene reference standards). Isotactic PMMA ($M_v = 2.5 \times 10^4$ g/mole, Polysciences, Inc.) was used without any purification. Chlorobenzene, methylene chloride and acetonitrile (HPLC grade) were used for the preparation of PMMA solutions. PMMA was dissolved in chlorobenzene and spin-coated onto silicone wafers and then baked at 150°C for 30 minutes to remove solvents completely.

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UV Irradiations and Structural Analysis

PMMA samples were exposed to light from a high pressure, 500 W, mercury-xenon lamp without a filter, in air. The intensity of UV light was measured with a Black-Ray[®] shortwave ultraviolet intensity meter J-225 (UVP, Inc., CA).

Irradiated PMMA samples on silicone wafers were dissolved in CDCl₃ and analyzed with a Varian 200 MHz proton magnetic resonance spectrometer (XL-200). From the ¹H NMR peak intensities of PMMA, which was studied,⁶ the content of rr, mr, mm triad sequences in Du Pont Elvacite 2041 was 63, 33, and 4 %, and for isotactic PMMA (Polysciences, Inc.) was 9, 21, and 70 %, respectively.

The most stable conformational isomers of model compounds for triads of MMA units were determined with the Macromodel program employing MM2 on a MicroVax II computer.⁷

RESULTS AND DISCUSSION

The characterization of unsaturated bonds generated in irradiated atactic PMMA films by ¹H NMR indicated that the major process leading to carbon double bonds is abstraction of a primary methyl hydrogen atom by an acyl fragment to yield vinylidene groups without main chain scission.³ This behavior is particularly apparent for UV irradiation where 90 % of the cleavage of methyl ester side chains is associated with the generation of vinylidene groups in the main chain despite the fact that reaction at the methylene sites is favored on enthalpic and statistical grounds.⁴

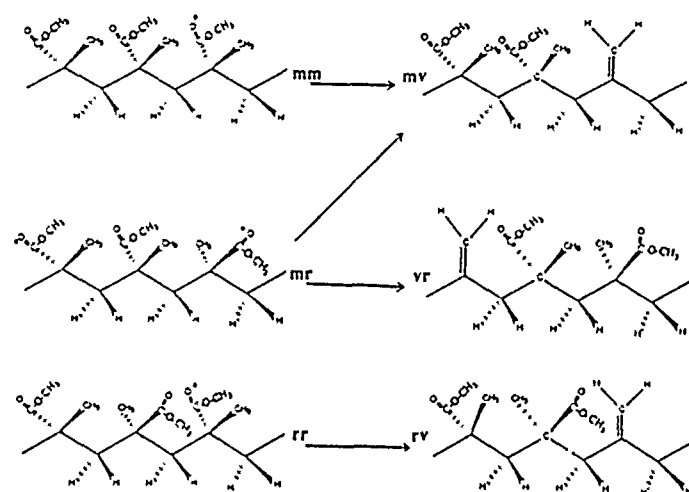
On formation of vinylidene groups (v) in the model sequences, the triad units, rr, mm and mr, give rise to two different types of segments (rv and mv) as shown in Scheme 1. In ¹H NMR spectra of the UV-irradiated atactic PMMA (Figure 1), the new peaks appear at 0.95 and 1.14 ppm. The relative height of these two peaks is approximately the same as the ratio of $rr+mr/2$ to $mm+mr/2$ triad contents, assuming that the mr triad has the same possibility to form mv or rv segments. These two peaks are assigned to α -methyl groups next to vinylidene groups: rv at 0.95 ppm and mv at 1.14 ppm.

In the most stable conformational isomers of the PMMA triad model compounds calculated with the Macromodel program,⁷ the hydrogen atoms of the α -methyl group are located much closer to carbonyl oxygen atom than to those of the methylene group in the rr and mr triad sequences, the content of which is 96% in atactic PMMA. This result may be one reason that the vinylidene group is the major segment produced in the UV-irradiated atactic PMMA film. In the structure of the mm triad model at the minimum energy state in the MM2 program, the carbonyl oxygen atom is positioned closer to the methylene hydrogen atoms than to the α -methyl hydrogen atoms. The amplified NMR spectra of UV-irradiated isotactic PMMA (Figure 2) shows several resonances of hydrogen atoms on unsaturated bonds with peaks appearing at 4.4-5.4 ppm, which are very similar to those in atactic samples, and the other peaks at 5.5-6.5 ppm are believed to originate from the degradation of isotactic segments.

When a solution of atactic PMMA in methylene chloride or acetonitrile was exposed to UV light, hydrogen atoms on unsaturated bonds, which are different from those generated in solid films, appeared in the ^1H NMR spectrum (Figure 2). This large difference may be explained by the fact that the degradation reaction occurs in a cage in the solid film at the most stable conformational structures. On the other hand, in solution, the cage effect and the probability of the degradation reaction occurring in the most stable conformational state is expected to be much diminished.

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Scheme 1. α -Methyl Groups in the Triad Sequences of Irradiated PMMA

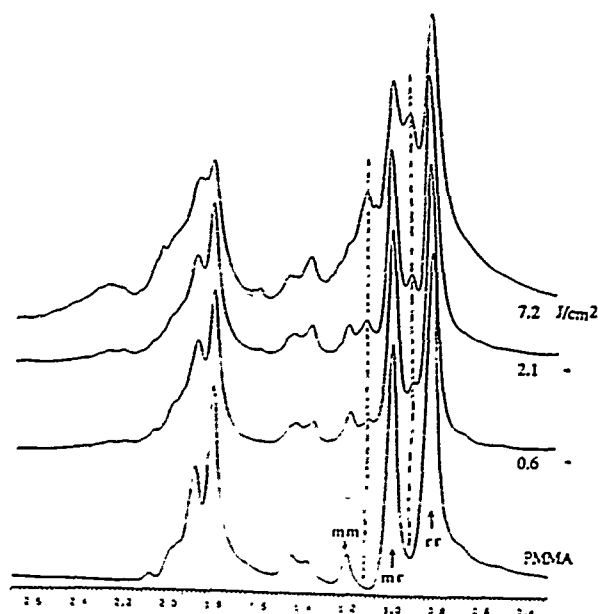


Figure 1. ^1H NMR Spectra ($\times 3$) of UV-Irradiated Atactic PMMA

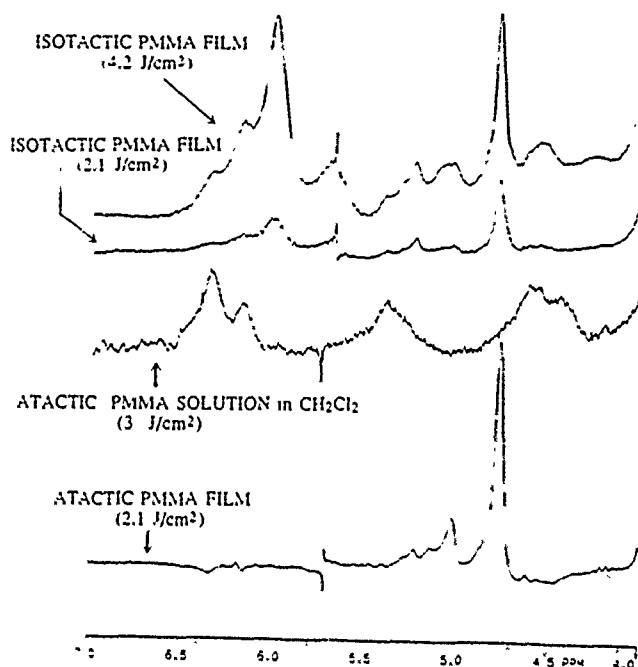


Figure 2. ^1H NMR Spectra ($\times 25$) of UV-Irradiated PMMA

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